

GHGT-10

Doped phenol-formaldehyde resins as precursors for precombustion CO₂ capture adsorbents

C.F. Martín, S. García, J.J. Pis, F. Rubiera, C. Pevida¹*Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain*

Abstract

The use of solid sorbents for precombustion CO₂ capture, which implies the removal of CO₂ from the shifted-syngas prior to electricity generation, has acquired increasing interest in recent years. As an alternative method for precombustion CO₂ capture, adsorption can be considered a promising technology, offering potential energy savings compared to absorbent systems. Solid sorbents are currently used in pressure swing adsorption (PSA) systems for the purification of hydrogen in petrochemical industries. In the present work, phenol formaldehyde resin-based adsorbents have been prepared to be applied in precombustion CO₂ capture applications. The produced carbons showed superior performance when compared to commercial CO₂ adsorbents and a great selectivity towards CO₂.

© 2011 Published by Elsevier Ltd.

Keywords: CO₂ adsorption, phenolic resins; precombustion capture

1. Introduction

Commercial methods to capture CO₂ have long been used in the chemical and petrochemical industries. These methods, applied to the removal of H₂S and CO₂ from gaseous streams, are mostly based on chemical absorption with aqueous solutions of alkanolamines (MEA, DEA, MDEA), in the case of combustion flue gases, or physical absorption with solvents (Rectisol®, Selexol®), in the case of high CO₂ partial pressures. However, these processes present several drawbacks such as high energy consumption, degradation, short life and high solvent cost [1]. Alternative methods have been proposed for CO₂ capture but, currently, advanced research is focused on membranes and adsorption with solid sorbents [2,3]. Adsorption is considered a promising technology for CO₂ capture applications since adsorbents present high adsorption capacity, great selectivity, good mechanical properties and they remain stable over repeated adsorption-desorption cycles [4,5]. Activated carbons are suitable candidates for CO₂ capture,

¹ Corresponding author. Tel.: +34 985 11 90 90; fax: +34 985 29 76 62.
E-mail address: cpevida@incar.csic.es

their adsorption performance being dependent on the pore structure and the properties of the surface chemistry [6]. Although capture capacities of activated carbons are, in general, lower than those of zeolites and molecular sieves under low pressure and ambient conditions, they present a series of advantages as CO₂ adsorbents such as larger capacities at higher pressures, ease of regeneration, potential low-cost and less sensitiveness to moisture. Phenolic-resin-based activated carbons offer further advantages in that they can be produced in a wide variety of physical forms (including granular or extruded, fibres, monolithic structures), allow close control of porosity, present a very low level of impurities and good physical strength [7,8].

In this work, phenol formaldehyde resins were synthesised with and without the addition of organic additives. These resins were carbonised and activated with CO₂ to produce phenolic-resin-based activated carbons. Samples were chemically and texturally characterised and their CO₂ capture performance evaluated under pure CO₂ flow (adsorption isotherms) and CO₂/H₂ mixtures (breakthrough curves).

2. Experimental

2.1. Synthesis of materials

In this work, phenol formaldehyde resin (PF) samples have been prepared following different synthesis pathways. During the synthesis, phenol and formaldehyde were mixed and heated in the presence of a catalyst. In some cases, an organic additive, ethylene glycol (EG) or polyethylene glycol (PEG), was also added. The following samples were produced: samples NA and CLA were synthesised without additive using NH₄OH and HCl, respectively, as catalyst; samples E1A and PE10 were prepared adding EG (1 wt.%) and PEG (10 wt.%), respectively, during the acid-catalysed synthesis route. Afterwards, the resins were cured in a rotary evaporator by heating under vacuum [9–12].

2.2. Carbonisation and activation with CO₂

The cured resins were then carbonised and activated with CO₂ to develop microporosity in the samples. Carbonisation was performed in a horizontal furnace up to 800°C under a stream of 50 mL min⁻¹ of N₂. Activation with CO₂ was conducted in a vertical furnace, in a flow rate of 10 mL min⁻¹ of CO₂ at 900°C. Activated carbons with various degrees of burn-off were prepared.

2.3. Characterisation

The obtained carbons were characterised in terms of texture and chemical composition. For the textural characterisation, the micropore volume, W_0 [13], the average micropore width, L_0 [14], and the BET surface area, S_{BET} (m²g⁻¹), were determined from the N₂ and CO₂ adsorption isotherms at 77 and 273 K, respectively.

Chemical characterisation involved proximate and ultimate analyses and evaluation of the point of zero charge (pH_{PZC}).

2.4. CO₂ capture capacity

The capture performance of the adsorbents was determined under pure CO₂ and CO₂/H₂ mixtures, to evaluate the equilibrium capacities and the maximum working capacities of the samples, respectively. CO₂ capture tests at 25°C and atmospheric pressure were conducted in a thermogravimetric analyser by recording the mass uptake of the samples when exposed to pure CO₂ atmosphere. High pressure CO₂ and H₂ adsorption isotherms were evaluated in a magnetic suspension balance at 25°C and pressures up to 30 (CO₂) and 40 bar (H₂). The maximum CO₂ uptakes of the samples at high pressures and their selectivity towards CO₂ were assessed.

The CO₂ capture performance of the adsorbents in a binary mixture of CO₂ and H₂ was also evaluated by obtaining the breakthrough curves of the samples in a purpose-built bench-scale system. The maximum working capacities were evaluated after seven consecutive adsorption-desorption cycles that involved an adsorption step at 15 bar and room temperature, followed by complete regeneration of the adsorbent at atmospheric pressure and 80 °C.

3. Results and discussion

3.1. Chemical analysis

Ultimate analysis and pH_{PZC} of the prepared carbons are included in Table 1. The main element in the samples composition is carbon (~97 wt.%). The obtained carbons show basic character ($\text{pH} > 7$), due to the devolatilisation of oxygenated compounds during carbonisation. Basicity also increased after activation with CO_2 , because part of the oxygen that was incorporated to the surface of the char during the activation step is in the form of basic oxygen groups (i.e., pyrone) [12,15].

Table 1 Chemical characterisation of the prepared adsorbents

Sample	Ultimate Analysis (wt.%, daf)				pH_{PZC}
	C	H	N	O*	
NA	97.3	0.3	0.9	1.5	8.8
CLA	97.4	0.1	–	2.5	9.4
E1A	97.2	0.1	–	2.7	8.8
PE10	95.7	0.1	–	4.2	7.5

O*: calculated by difference

3.2. Textural characterisation

Table 2 summarises the textural parameters calculated from the N_2 and CO_2 adsorption isotherms at 77 and 273 K, respectively, and the helium density of the PF carbons.

Helium density in PF samples is around 2 g cm^{-3} . Activation with CO_2 resulted in a significant textural development. The prepared carbons are mainly microporous. BET surface areas (S_{BET}) and total micropore volumes ($W_{0\text{N}_2}$) are similar for the activated samples, but lower for the carbonised sample PE10. Analysing the narrow microporosity in the PF carbons, here assessed by the CO_2 adsorption isotherms, differences between the activated samples can be observed. E1A shows the highest narrow micropore volume ($W_{0\text{CO}_2}$) ($0.33 \text{ cm}^3 \text{ g}^{-1}$), most probably as a consequence of the addition of EG during the synthesis. Regarding the average narrow micropore widths ($L_{0\text{CO}_2}$), the activated samples present average values around 0.7 nm while sample PE10 exhibits the smallest average narrow micropore width.

Table 2 Textural parameters calculated from the N_2 and CO_2 adsorption isotherms of PF carbons

Sample	d_{He} (g cm^{-3})	N_2 adsorption at 77 K		CO_2 adsorption at 273 K	
		S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	$W_{0\text{N}_2}$ ($\text{cm}^3 \text{ g}^{-1}$)	$W_{0\text{CO}_2}$ ($\text{cm}^3 \text{ g}^{-1}$)	$L_{0\text{CO}_2}$ (nm)
NA	2.08	1211	0.45	0.26	0.70
CLA	2.11	1381	0.51	0.29	0.74
E1A	1.96	1369	0.51	0.33	0.73
PE10	1.92	472	0.25	0.23	0.58

Since the molecular size of CO_2 is 0.209 nm, only pores less than 1.0 nm are effective towards CO_2 capture at atmospheric pressure. Thus, the textural characterisation suggests that the produced carbons present suitable porous structure to be applied as CO_2 adsorbents.

3.3. CO_2 capture capacity

Figure 1 shows the CO_2 uptake for each sample at 298 K and atmospheric (1 bar) and high pressure (30 bar). CO_2 capture capacities are expressed in mmol of CO_2 per gram of adsorbent (mmol g^{-1}). These values correspond to the equilibrium CO_2 uptakes under the tested conditions. Figure 1 shows the

correlation between the CO₂ uptakes and the total micropore (W_{0N_2}) and narrow micropore (W_{0CO_2}) volumes.

The maximum CO₂ uptake at atmospheric pressure was achieved by sample E1A, 2.46 mmol g⁻¹, closely followed by samples CLA and NA that reached 2.16 and 2.07 mmol g⁻¹, respectively (see Figure 1). These values are comparable or slightly superior to those assessed on commercial activated carbons [4,16-18].

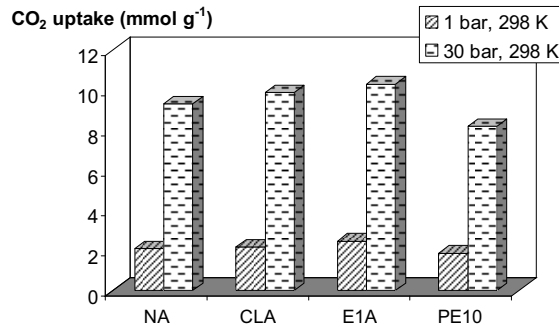


Figure 1. CO₂ uptakes (mmol g⁻¹) at 298 K, and 1 and 30 bar, respectively.

At 30 bar, the maximum CO₂ uptake corresponded to E1A that reached 10.30 mmol g⁻¹, followed by CLA, 9.89 mmol g⁻¹. High-pressure CO₂ capture capacities are greater than those of commercial CO₂ adsorbent materials like zeolite 13X (7.4 mmol g⁻¹ at 32 bar and 298 K [19]) or BPL carbon (8.4 mmol g⁻¹ at 55 bar and 298 K [20]).

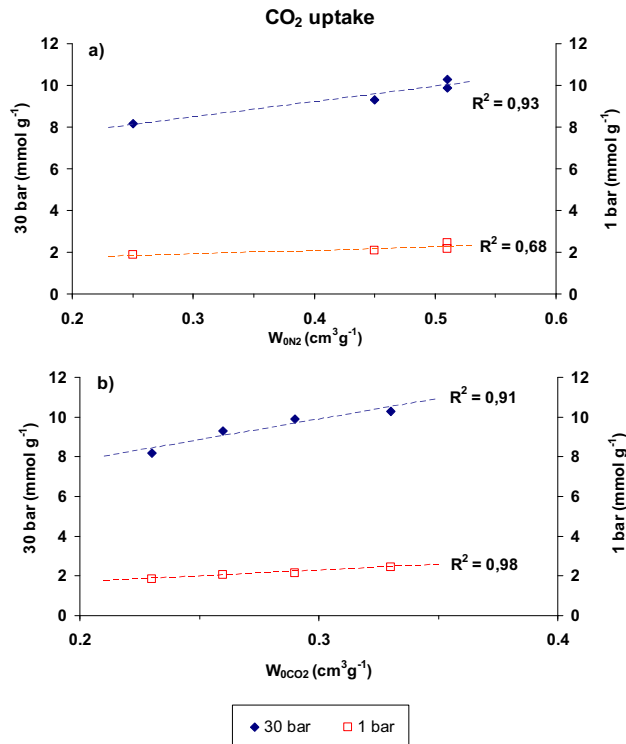


Figure 2. Correlation between the CO₂ uptakes at 1 and 30 bar, and W_{0N_2} (a) and W_{0CO_2} (b).

On the other hand, the carbonised sample, PE10, presented the lowest CO₂ uptakes: 1.86 and 8.18 mmol g⁻¹ at 1 and 30 bar, respectively.

Relating the results of these tests to the textural characteristics of the adsorbents (see Figure 2) it can be observed that there is a good correlation between CO₂ uptake and narrow micropore volume ($W_{0\text{ CO}_2}$). In the particular case of CO₂ adsorption at atmospheric pressure, the higher $W_{0\text{ CO}_2}$, the greater the CO₂ uptake (Figure 2b). At high pressure there is also a good correlation between the CO₂ uptake and the total micropore volume ($W_{0\text{ N}_2}$) that, on the other hand, does not exist at atmospheric pressure (see R^2 in Figure 2a). At atmospheric pressure the presence of narrow microporosity plays a key role on the CO₂ adsorption performance. However, at higher pressures, CO₂ is also adsorbed on the super-microporosity range (pore sizes between 0.7 and 2 nm). In addition, these correlations show that it is possible to assess the maximum CO₂ adsorption capacity of an adsorbent from its textural characterisation [17].

It is worth to draw attention on sample PE10 that shows a CO₂ uptake at atmospheric pressure comparable to the activated resins. This may be due to the organic additive (PEG) that enhances narrow microporosity development.

The CO₂ capture performance of sample E1A in a ternary mixture containing 20–40 vol.% of CO₂ and 50–70 vol% H₂ (N₂ balance), was also evaluated. The values of CO₂ adsorption capacities shown in Table 3, were obtained from the average capacity of seven consecutive breakthrough curves.

Table 3 CO₂ capture capacities of E1A at ambient temperature and 15 bar in CO₂/H₂/N₂ mixtures

Cases	P (bar)	T (K)	CO ₂ (vol%)	H ₂ (vol%)	CO ₂ capture capacity (mmol CO ₂ g ⁻¹)
1	15	298	20	70	4.57
2	15	298	40	50	6.14

CO₂ adsorption capacity is reduced when the partial pressure of CO₂ is diminished, as expected for conventional adsorption processes. According to the high pressure CO₂ adsorption isotherms, the maximum CO₂ uptake of E1A was 4.77 mmol g⁻¹ at 3 bar and 6.45 mmol g⁻¹ at 6 bar. Cases 1 and 2 correspond to CO₂ partial pressures in the feed stream of 3 and 6 bar, respectively. Thus, the CO₂ capture capacities assessed during these experiments are close to those of the equilibrium, showing the great selectivity of the carbon towards CO₂.

4. Conclusions

Addition of organic additives, ethylene or polyethylene glycol, during the synthesis of phenol-formaldehyde resins enhanced the textural characteristics of the prepared activated carbons. The CO₂ capture performance of the phenol-formaldehyde resin-based carbons showed promising results at atmospheric and high pressures, when compared to commercial CO₂ adsorbents. In addition, it has been demonstrated that CO₂ adsorption relies on both the width and volume of micropores. The sample produced with addition of ethylene glycol, E1A, reached the greatest CO₂ uptakes (2.46 mmol g⁻¹ at atmospheric pressure and 10.30 mmol g⁻¹ at 30 bar). Great selectivity of the carbons to separate CO₂ from CO₂/H₂ mixtures was observed.

From the results presented here it can be concluded that phenol-formaldehyde resin carbons show promising characteristics to be applied in precombustion CO₂ capture processes. Further research is currently being undertaken in our research group to tailor and improve the characteristic of these resin adsorbents, without increasing the cost of the production process.

5. Acknowledgements

This work was carried out with financial support from the Spanish MICINN (Project ENE2008-05087). C.F.M. acknowledges support from the CSIC JAE-Predoc Program.

6. References

- [1] IEA, International Energy Agency Report. Capturing CO₂. 2007
- [2] Figueroa JD, Fout T, Plasynski S, McIlvried H, Srivastava RD. Advances in CO₂ capture technology—The U.S. Department of Energy's Carbon Sequestration Program. *Int. J. Greenh. Gas Con.* 2008; 2: 9-20
- [3] Drage TC, Blackman JM, Pevida C, Snape CE. Evaluation of activated carbon adsorbents for CO₂ capture in gasification. *Energ. Fuel.* 2009; 23: 2790-6
- [4] Yong Z, Mata V, Rodrigues AE. Adsorption of carbon dioxide at high temperature—a review. *Sep. Purif. Technol.* 2002; 26: 195-203
- [5] Choi S, Drese JH, Jones CW. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. *ChemSusChem* 2009; 2: 796-854
- [6] Sircar S, Golden TC, Rao M.B. Activated carbon for gas separation and storage. *Carbon* 1996; 34: 1-12
- [7] Foster AI, Linney HJ, Tennison SR, Cory RA, Swan DP. The use of carbons produced from phenolic resins for flue gas desulphurization. *Fuel* 1993; 72: 337-42
- [8] Tennison SR. Phenolic-resin-derived activated carbons. *Appl. Catal. A-Gen.* 1998; 173: 289-311
- [9] Chi-Cheng L, Teng H. Influence of the formaldehyde-to-phenol ratio in resin synthesis on the production of activated carbons from phenol-formaldehyde. *Ind. Eng. Chem. Res.* 2002; 41: 1986-92
- [10] Horikawa T, Ogawa K, Mizuno K, Hayashi J, Muroyama K. Preparation and characterization of the carbonized material of phenol-formaldehyde resin with addition of various organic substances. *Carbon* 2003; 41: 465-72
- [11] Shafizadeh JE, Guionnet S, Tillman MS, Seferis JC. Synthesis and characterization of phenolic resole resins for composite applications. *J. Appl. Polym. Sci.* 1998; 73: 505-14
- [12] Teng H, Wang S-C. Preparation of porous carbons from phenol-formaldehyde resins with chemical and physical activation. *Carbon* 2000; 38: 817-24
- [13] Dubinin MM. Fundamentals of the theory of adsorption in micropores of carbon adsorbents: Characteristics of their adsorption properties and microporous structures. *Carbon* 1989; 27: 457-67
- [14] Stoeckli F, Ballerini L. Evolution of microporosity during activation of carbon. *Fuel* 1991; 70: 557-9
- [15] Papirer E, Li S, Donnet J-B. Contribution to the study of basic surface groups on carbons. *Carbon* 1987; 25: 243-7
- [16] Pevida C, Plaza MG, Arias B, Feroso J, Rubiera F, Pis JJ. Surface modification of activated carbons for CO₂ capture. *Applied Surface Science* 2008; 254: 7165-72
- [17] Martín CF, Plaza MG, Pis JJ, Rubiera F, Pevida C, Centeno TA. On the limits of CO₂ capture capacity of carbons. *Sep. Purif. Technol.* 2010; 74: 225-9
- [18] Plaza MG, García S, Rubiera F, Pis JJ, Pevida C. Post-combustion CO₂ capture with a commercial activated carbon: comparison of different regeneration strategies. *Chem. Eng. J. In Press.*
- [19] Millward AR, Yaghi OM. Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature. *J. Am. Chem. Soc.* 2005; 127: 17998-9
- [20] Furukawa H, Yaghi OM. Storage of hydrogen, methane, and carbon dioxide in highly porous covalent organic frameworks for clean energy applications. *J. Am. Chem. Soc.* 2009; 131: 8875-83